Title	1963 : Organic Chemistry
Author(s)	
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1964), 41(5-6): 272-276
Issue Date	1964-02-25
URL	http://hdl.handle.net/2433/75976
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Organic Chemistry

Reaction of alkyl phenyl ketones with nitrosylsulfuric acid. Yoichiro Ishikawa, Masaya Okano and Ryohei Oda. *Kogyo Kagaku Zasshi,* **66,** 1314 (1963), in Japanese.—The reaction of nitrosylsulfuric acid with cyclohexyl aryl ketones in oleum (the SNIA process) was extended to alkyl phenyl ketones. Besides benzoic acid, the corresponding ketoxime or acid amides were obtained in 20-30% yields. The reaction with a ketone having a branch on α-carbon such as isopropyl phenyl ketone gave a ketoxime. On the other hand, the same reaction with n-alkyl phenyl ketones (e. g. n-pentadecyl phenyl ketone) gave the corresponding acid amides which probably resulted from dehydration of adoximes, followed by hydrolysis.

New addition reactions. V. Dimerization of diketene. Ryohei Oda, Shunichi Takashima and Masaya Okano. *Bull. Chem. Soc. Japan,* **36,** 476 (1963).—See, this Bulletin, **41,** 233 (1963).

Kinetics of the reaction of N-arylpyridinium chloride with anilines. Ryohei Oda and Shinji Mita. *Bull. Chem. Soc. Japan,* **36,** 103 (1963).—The rates of the reaction of 2, 4-dinitrophenylpyridinium chloride with ring-substituted anilines in methanol have been estimated by the gravimetry of the produced glutacondialdehyde dianil. The rates have been found to be second-order with aniline and first-order with pyridinium salt. The electron-withdrawal groups in pyridine accelerate the reaction. These facts suggest a mechanism involving a nucleophilic attack of the molecules of aniline on a complex consisting of 2 molecules of aniline and a pyridinium ion. The products of the reaction of 2, 4, 6-trinitrophenylpyridinium chloride with aniline were 2, 4, 6-trinitrodiphenylamine and the dianil.

The reactions of dichloromethyl methyl ether with diarylether type compounds and with Grignard reagents. Ryohei Oda and Keiji Yamamoto. *Nippon Kagaku Zasshi,* **84,** 348 (1963), in Japanese.—Aromatic aldehyde synthesis using dichloromethyl ether [A. Rieche, et. al., *Chem. Ber.,* **93,** 88 (1960)] failed to prepare the dialdehyde of Ar-X-Ar′ (X : O, S) type compounds, and the reaction products were the corresponding monoaldehyde (yield, 25 %) and xanthone (16 %) or thioxanthone (26 %) respectively. This may be one of Friedel-Crafts type reaction, but the mechanism is not clear. In the reaction of dichloromethyl methyl ether with various Grignard reagents (six halides were used), the major product was the methylether of seconday carbinol (yield, 38~73 %), and at the same time a small amount of aldehyde (trace-14 %) was also obtained in every case.

Reactions of α, β-unsaturated carbonyl-compounds with thiourea. Shigeo Tanimoto, Kaichi Murao and Ryohei Oda. *Kogyo Kagaku Zasshi,* **66,** 48 (1963), in Japanese.—It is already known that the thiourea (I) reacts with such α, β-unsaturated carbonyl-compounds as acrylonitrile, acrylamide, and α-vinylpyridine in the presence of acidic catalyser to give the following isothiouronium salt :

$$NH_2CSNH_2 + CH_2{=}CH{-}\overset{|}{C}{=}O \xrightarrow{HX} \left[\begin{matrix} NH_2 \\ \diagdown \\ \quad C{-}S{-}CH_2{-}CH_2{-}\overset{|}{C}{=}O \\ \diagup \\ NH_2 \end{matrix}\right]^{\oplus} X^{\ominus}$$

The authors also investigated the analogous reaction, using ethyl acrylate, divinylsulfone, ethyl maleate and N-dodecylmaleimide as the α, β-unsaturated carbonyl-compound and obtained the following results: Ethyl acrylate, thiourea, and *p*-toluene sulfonic acid containing one water molecule of crystallization were reacted in the boiling and refluxed ethyl alcohol and the reacted liquid mass, after removing ethyl alcohol by means of vacuum, was poured into ether giving *S*-(β-ethoxycarbonylethyl)-isothiouronium-*p*-toluenesulfonate which had the melting point of 89~92 °C. Divinylsulfone, thiourea, and *p*-toluenesulfonic acid having one water molecule of crystallization were reacted in the boiling and refluxed ethyl alcohol giving diethylsulfone-*bis*-*S*-isothiouronium-*p*-toluenesulfonate which had the melting point of 197 ~ 200 °C. Maleic anhydride, thiourea, and *p*-toluenesulfonic acid were reacted in the boiling and refluxed ethyl alcohol. By removing a part of ethyl alcohol by vacuum distillation, 2-imino-4-oxo-5-thiazolidineacetic ester *p*-toluenesulfonate (IV) which had a melting point of 187 ~ 189 °C. Diethyl maleate, thiourea, and *p*-toluenesulfonic acid were reacted in the boiling and refluxed ethyl alcohol. The substance IV was obtained by removing a part of ethyl alcohol by vacuum distillation. It showed the melting point of 188.5 ~ 190.5 °C. By reacting *N*-dodecyl maleimide, thiourea, and *p*-toluene sulfonic acid having one water molecule of crystallization in the boiling and refluxed ethyl alcohol. *S*-(*N*-dodecylsuccinimide)-isothiouronium-*p*-toluenesulfonate was obtained. Its melting point was 147.5 ~ 149.5 °C.

A kinetic study of the reaction of ethylene carbonate and amines. Iwao Tabushi and Ryohei Oda. *Nippon Kagaku Zasshi*, 84, 162 (1963), in Japanese.—Rates of the reactions of ethylene carbonate with various primary amines were measured by determining the amounts of the unreacted amines with perchloric acid. Reaction products were corresponding linear carbamates, $RNHCO_2CH_2CH_2OH$, except in the case of 2-aminoethanol, where oxazolidinone-2 was obtained according to the condition. The rate of reaction with 2-aminoethanol was proportional to the concentration of 2-aminoethanol, while the rates of reaction with other amines can be expressed as $v = k$ [amine] $[\text{amine}]_0^n$ [ethylene carbonate], where $[\text{amine}]_0$ is the initial concenation of an amine and the value of n turned out to be equal to or larger than unity. Carbamate, the products, catalyses the reaction. The rate equation suggests that amines, the reactants, also have a catalytic action. Relation between reactivity and structure of amines cannot be explained in terms of the polar and steric effects of substituents (Taft's eqation) alone, but it is explained satisfactorily by introducing an additive hyperconjugation effect of α-CH groups of amines in the electron deficient reaction.

Some applications of the *bis*-chloromethylated *p*-xylene and diphenyl ether. Kaichi Murao, Shigeo Tanimoto and Ryohei Oda. *Kogyo Kagaku Zasshi*, **66**, 1538 (1963), in Japanese.—*p*-Xylene and diphenyl ether were *bis*-chloromethylated, respectively and α^1, α^4-dichlorodurene and 4, 4′-*bis*-chloromethyl-diphenyl ether, thus obtained, were condensed with phenol and new kinds of bisphenols were obtained. Form these two bisphenols, epoxy-resin, polycarbonate resin and also polyester resin were prepared. Among these new synthetic resins, some epoxy-

resin and some polyester resins, prepared from the new bisphenols and isophthalyl chloride by the interfacial technique, were found to be promising for practical uses from their properties. A kind of redox resin (electron exchange resin) was prepared by condensing the new bisphenol with hydroquinone, but its exchange capacity was rather poor.

Bis-chloromethylation of 1, 2-diphenoxyethane and polycondensation of the chloromethylated compounds by Friedel-Crafts catalysis. Iwao Tabushi, Kunihiko Takagi, Shiro Nagata and Ryohei Oda. *Kogyo Kagaku Zasshi*, **66,** 979 (1963), in Japanese.—In order to obtain *bis*-chloromethyl-1, 2-diphenoxyethane, *bis*-chloromethylation of 1, 2-diphenoxyethane was investigated under various conditions and it was found that the diphenoxyethane could be smoothly *bis*-chloromethylated by paraformaldehyde and hydrogen chloride gas in acetic acid in the presence of phosphoric acid as a catalyst. So far as here investigated, other conditions did not give good yield of the aimed products, but resulted in the production of undesired highly condensed compounds. Chloromethylated diphenoxyethane thus obtained gave readily polycondensation products when treated with Friedel-Crafts catalysts. A convenient method of preparation of diphenoxyethane from phenol and ethylene chloride in aqueous alkaline solution was also investigated.

Chemistry of the addition compounds of mercuric salts with olefins. Katsuhiko Ichikawa. *Kogyo Kagaku Zasshi*, **66,** 1037 (1963), in Japanese.

Reaction of methylene with methyl isopropyl ether. Tadashi Inoue and Yoshimasa Takezaki. *Bull. Inst. Chem. Res., Kyoto Univ.*, **41,** 190 (1963).

A convenient synthetic method of certain aromatic polyiodo compounds. Hitomi Suzuki and Ryozo Goto. *Bull. Chem. Soc. Japan*, **36,** 389 (1963).—A convenient synthetic method of certain aromatic polyiodo compounds, based on the migration, in the presence of sulfuric acid, of iodine atoms present in the nucleous of aromatic iodo compounds (Jacobsen reaction), has been proposed. This method is especially attractive to the synthesis of symmetrically substituted or fully iodinated compounds. With the aid of this simple method, about twenty polyiodo compounds have been prepared.

On the Jacobsen reaction of polyhalogenobenzenes and monoalkylpolyhalogenobenzenes. Ryozo Goto and Hitomi Suzuki. *Nippon Kagaku Zasshi*, **84,** 167 (1963) in Japanese.—Investigations of the Jacobsen reaction have been carried out with the following compounds : polyiodobezenes ; polybromobenezenes ; polychlorobenezenes ; monohalogen derivatives of toluene, ethylbenzene, cumene and *tert*-butylbenzen polyiodotoluenes. Intermolecular migration of halogen atoms is usually observed only with bromo and iodo compounds. Reactions, in most cases, proceed as a progressive halogenation of an original material and lead to mixtures of polyhalogenated products in which no tendency toward vicinal orientation is observed. Some iodobenzene derivatives with three substituents in vicinal position show anomalous reactions. Inductive and steric effects of substituents have a

definite influence on a course of the reaction and determine the nature as well as the ease with which the migration takes place. The reaction is considered of much value for the direct syntheses of some polyiodo compounds.

On the Jacobsen reaction of polyhalogenobenzenes and other related halogeno compounds. Hitomi Suzuki and Ryozo Goto. *Nippon Kagaku Zasshi,* Investigations of the Jacobsen reaction have been carried out with the following compounds : monohalogenoxylenes ; *sym*-dihalogenoxylenes ; monohalogen derivatives of trimethylbenzenes, triethylbenzenes, tetramethylbenzenes and tetraethylbenzenes; halogenophenols and halogenoanisols. Inductive, mesomeric and steric effects of substituents and their relative positions in the nucleus determine whether or not a reaction will take place. Increase of the number of alkyl groups favors both migration of halogen atoms and formation of resinous materials. With chlorine compounds, intramolecular migration of halogen atom occurs whereas with iodine, intermolecular migration takes place. With bromine, however, both types of reaction occur simultaneously. Vicinal orientation, an important characteristic of the reaction, is observed only with a compound of particular structure. With symmetrically substituted polyalkylhalogenobenzenes, an attempt has been made to indicate the condition at which vicinal orientation takes place. The reaction is of practical value for the convenient syntheses of otherwise inaccessible vicinal compounds.

On the Jacobsen reactions of polyhalogenobenzenes. Hitomi Suzuki and Ryozo Goto. *Nippon Kagaku Zasshi,* **84,** 435 (1963), in Japanese.—The Jacobsen reaction has been studied with twelve tetraalkylbenzenes, two pentaalkylbenzenes and eight dialkyltetralins. Steric and inductive effects of alkyl groups determine the course of the reaction and the ease with which it takes place. With tetra or pentaalkylbenzenes having tetramethylene rings or alkyl groups of short, straight chains, such as methyl, ethyl and *n*-propyl, the Jacobsen reaction appears to be rather extensive reaction while with those having alkyl groups of branched structure, such as isopropyl and *tert*-butyl, eliminations of these or other alkyl groups are the only reactions taking place. Besides vicinal tetraalkylbenzenes, in all experiments, small amounts of hexaalkylbenezene and trialkylbenezenes resulted from alkyl group migrations, and substantial amounts of unidentified tarry materials were formed. Plyalkylbenzenes having several alkyl groups of different structures afford reaction mixtures composed of os many kinds of hydrocarbons, from which pure products can be separated only with diffculty. The Jacobsen reaction, therefore, cannot be considered as the universal synthetic method of vicinal tetraalkylbenzenes. Investigations were carried out by the aid of gas chromatography as well as infrared spectroscopy, and some errors found in previous works were pointed out. The mechanism of the reations is briefly discussed based on the obtained experimental data.

Mass spectra of seven isomeric hexen-1-ols. E. Honkanen, T. Moisio, Minoru Ohno and Akikazu Hatanaka. *Acta Chemica Scandinavica,* **17,** 2051 (1963).—Mass

spectra of seven isomeric hexen-1-ols have been determined in order to detect any correlations between fragmentation patterns and molecular structure. The double bond isomers have proved to be easily recognizable by their different base peaks. The mass spectra of the corresponding cis and trans isomers are in general very similar. Some differences between the spectra of the geometric isomers of 2- and 3-hexen-1-ols exist, however, which are sufficient for qualitative analysis. Gas chromatographic retention times for the isomeric hexen-1-ols are given.

Studies on the alkaloids of Thalictrum Thunbergii DC. XIV. Structures of thalicberine and O-methylthalicberine. (6). Eiichi Fujita, Toshiaki Tomimatsu and Yoko Kano. *Yakugaku Zasshi*, **83**, 160 (1963) in Japanese.—In order to elucidate the structure of the substance III, derived from the basic decomposition product of ozone oxidation of O-methylthalicberine methylmethine (I), synthesis of 2-methoxy-4-methyl-5-ethylphenyl 2-methyl-3-ethyl-5, 6-dimethoxyphenyl ether (II) was carried out. One of the starting materials, 3-bromo-4-methyl-5-ethyl-1, 2-dimethoxybenzene (VIII), was synthesized form isovanillin (III) by its Clemmensen reduction to IV, introduction of acetyl group by the Friedel-Crafts reaction, Clemmensen reduction of its products to VI, bromination to VII, and finally by O-methylation to VIII. The other substance XVI was synthesized from *m*-cresol (IX) by its acetylation to X, Fries rearrangement followed by Clemmensen reduction to XII, and O-methylation to 3-methyl-4-ethylanisole (XIII), which was reduced and hydroxyl group introduced through diazotization. The position of this hydroxyl group was confirmed through the negative Gibbs reaction and identity of the infrared spectrum (in $CHCl_3$) of the O-methyl ether (XVII) of this substance with that of O-methyl ether (XVII) of VI synthesized by a known method. The Ullmann condensation of these 3-bromo-4-methyl-5-ethyl-1, 2-dimethoxybenzene (VIII) and 2-methoxy-4-methyl-5-ethylphenol (XVI) gave the desired substance (II).

The alkaloids of American lotus, Nelumbo Lutea. S. M. Kupchan, B. Dasgupta, E. Fujita and M. L. King. *Tetrahedron*, **19**, 227 (1963).—The leaves and stems of Nelumbo lutes (Willd.) Pers. from Wisconsin yielded the alkaloids nuciferine, (±)-armepavine, and two apparently new alkaloids to which we have assigned structures V ((−)-N-norarmepavine) and XII ((−)-N-nornuciferine).

Biochemistry

Biosynthesis of S-methyl-L-cysteine and S-methyl-L-cysteine sulfoxide from methionine in garlic. Michiyasu Sugii, Shigeharu Nagasawa and Tomoji Suzuki. *Chem. Pharm. Bull. Japan*, 11, 135 (1963).—An excised aerial part of garlic plant was cultivated in water containing L-methionine ^{35}S. After 24 hours' feeding the amino acid, a fraction was extracted from the plant and ^{35}S-labeled amino acid were separated by paper chromatography and Dowex 50 column. Methionine, methionine sulfoxide, S-methyl-L-cysteine and S-methyl-L-cysteine sulfoxide were obtained, but no other radioactive amino acids was detected in this experiment.